REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE 31 December 1998	3. REPORT TYPE AND DATES COVERED Progress Report: 1 Oct 98 - 31 December 98

4. TITLE AND SUBTITLE
Processing of Nanocrystalline Nitrides and Oxide Composites

5. FUNDING NUMBERS
G - N00014-95-1-0626

6. AUTHORS
Jackie Y. Ying
Martin L. Panchula

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemical Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Room 66-544
Cambridge, MA 02139-4307

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Ballston Tower One
Arlington, VA 22217-5660

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

We have recently begun to investigate the chemical composition, specifically oxygen contamination, and sintering behavior of the nanocrystalline aluminum nitride synthesized in the forced flow reactor. Our initial results from these studies show that nanocrystalline aluminum nitride can be produced with high purity (<4 wt% oxygen), and that full densification can be achieved without the use of sintering aids. In addition, hot pressed compacts of nanocrystalline aluminum nitride show an unusual degree of texturing after sintering, which may make these materials interesting for piezoelectric as well as thermal applications.

14. SUBJECT TERMS
Nanocrystalline, Aluminum Nitride, Texturing, Sintering, Piezoelectric

15. NUMBER OF PAGES
4

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

"Processing of Nanocrystalline Nitrides and Oxide Composites"

Technical Report on ONR Grant No. N00014-95-1-0626
for the period of October 1, 1998 - December 31, 1998

Jackie Y. Ying
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-544, 77 Massachusetts Avenue
Cambridge, MA 02139-4307
Tel: (617) 253-2899
Fax: (617) 258-5766

Nanocrystalline Aluminum Nitride

We have recently begun to investigate the chemical composition, specifically oxygen contamination, and sintering behavior of the nanocrystalline aluminum nitride synthesized in the forced flow reactor. Our initial results from these studies show that nanocrystalline aluminum nitride can be produced with high purity, and that full densification can be achieved without the use of sintering aids. In addition, hot-pressed compacts of nanocrystalline aluminum nitride show an unusual degree of texturing, which may make these materials interesting for piezoelectric as well as thermal applications.

Oxygen Analysis

Oxygen analyses of as-synthesized and sintered nanocrystalline AlN samples have recently been performed by fast neutron activation analysis (FNAA). The as-prepared sample had 3.9 wt% oxygen, and the sample which had been pressureless sintered at 1900°C had 2.7 wt% oxygen. The lower oxygen content of the sintered specimen is probably due to the loss of aluminum oxides, which can occur at temperatures above 1700°C. These oxygen analysis results are quite promising since commercial microcrystalline aluminum nitride powders with significantly lower surface areas contain up to 2 wt% oxygen. A better comparison of these materials might be made with the nanocrystalline aluminum nitride prepared by A.C. Da Cruz et al. [1], which contained approximately 25 wt% oxygen due to the high surface areas (85 m^2/g) and the lack of air-free handling prior to sintering. The samples prepared by us have approximately 3 times the surface area of Da Cruz's powders, but contain nearly 10 times less oxygen. This suggests that our processing methods have prevented oxygen contamination to a great extent. However, more work in process purification may be needed to allow additive-free densification of high thermal conductivity aluminum nitride.

Preliminary Sintering Studies

Two densification methods, hot pressing and pressureless sintering, are currently being explored to determine the best way of sintering nanocrystalline aluminum nitride. The first step in these preliminary sintering experiments was to examine the effect of pressure on the densification of nanocrystalline aluminum nitride powder. Nanocrystalline AlN was loaded into a graphite die inside the glovebox, and then quickly transferred to the hot press where it was evacuated and backfilled with 99.999% pure nitrogen three times. The uniaxial load was then applied and the furnace was heated at 25°C/min under a flow of 1 liter/min N_2 to the sintering temperature of 1900°C. Other researchers have reported that there is a strong dependence of densification on pressure, grain size, and oxygen content for aluminum nitride [2,3]. As shown in Figure 1, we observed an increase of 12% in the final density between 10 and 50 MPa, while there is only a 6% increase as the pressure is increased from 50 to 100 MPa. The pellets obtained from this experiment have picked up a considerable amount of carbon during the hot pressing (giving them a dark color), which may be limiting their densification. This hypothesis is supported by the work of Kurokawa et al. [4] who found that as little as 1 wt% carbon made densification above 70% very difficult during hot pressing. This problem will be mitigated in future studies by using graphite dies that are coated with boron nitride for the hot pressing experiments.

An interesting side-effect of hot pressing the nanocrystalline aluminum nitride is that significant texturing can occur (see Figure 2). The samples shown in Figure 2 were hot pressed to 1900°C at 25°C/min under 50 MPa with a one-hour dwell. The nanocrystalline sample appears to have a large fraction of the grains aligned with the normal of the (001) plane parallel to the pressing direction. This effect is not observed during the hot pressing of microcrystalline aluminum nitride. There are two probable reasons for the texturing observed in our nanocrystalline AlN samples. The first, and most likely cause, is that some of the plate-like particles (shown in Figure 3) produced during nanoparticle synthesis undergo alignment due to the pressing motion. During sintering and grain growth this alignment is locked in and results in the observed texturing. The second possibility, which may occur concomitantly with the first, is that the AlN nanocrystallites may undergo plastic deformation at these high temperatures and pressures, resulting in an alignment of the grains. This method may be thought of as similar to the way that drawn metal wires become textured. The texturing may be of significant interest for piezoelectric applications. Other researchers have attempted to produce bulk textured AlN by seeding the AlN with SiC platelets and annealing it for long periods (1-15 hr) [5]. The degree of orientation that was achieved by this seeding technique appears to be significantly lower than that obtained in our case. We will be performing a more detailed texture analysis to determine the amount and angle of alignment relative to the pressing direction. Future studies will seek to determine the degree of orientation and the mechanism through which it occurs, so as to develop and optimize a method for producing bulk textured AlN.

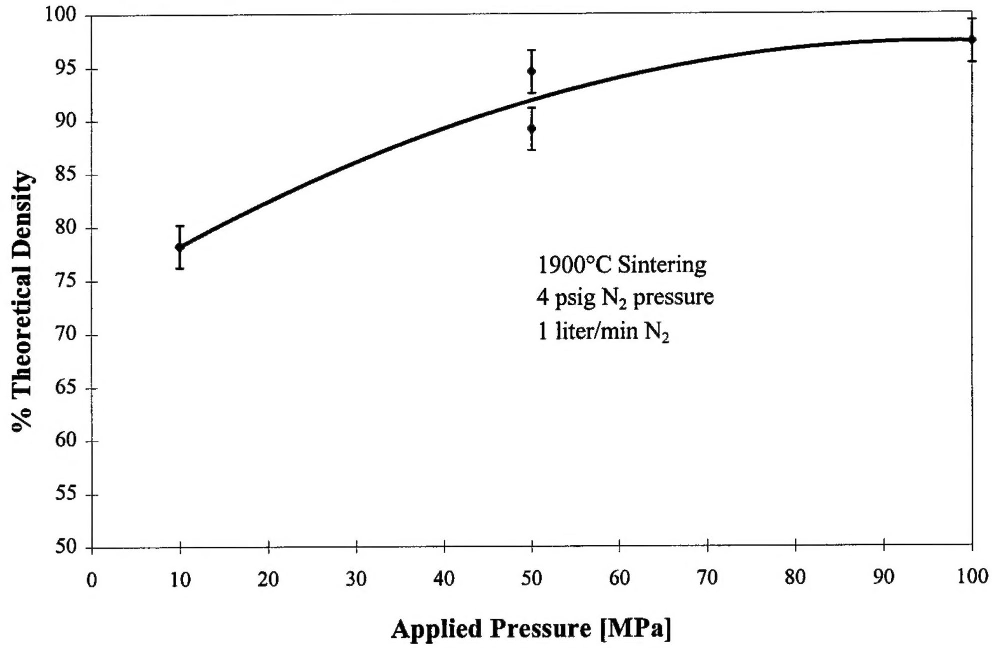

Figure 1. Densification of nanocrystalline aluminum nitride via hot pressing.

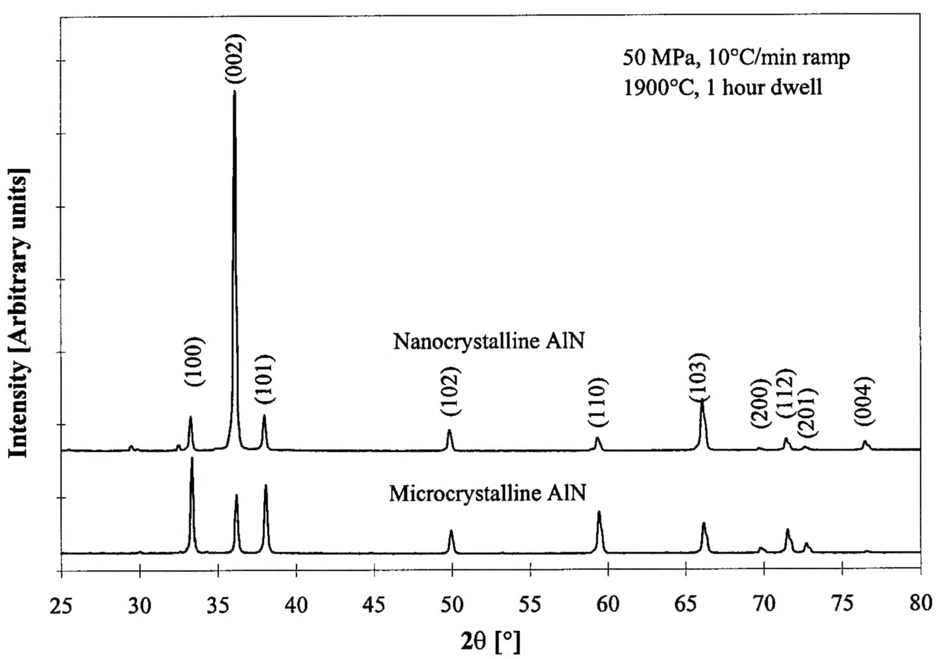

Figure 2. X-ray diffraction patterns of hot pressed nanocrystalline and microcrystalline AlN. Diffraction patterns were taken of polished surfaces perpendicular to the pressing direction.

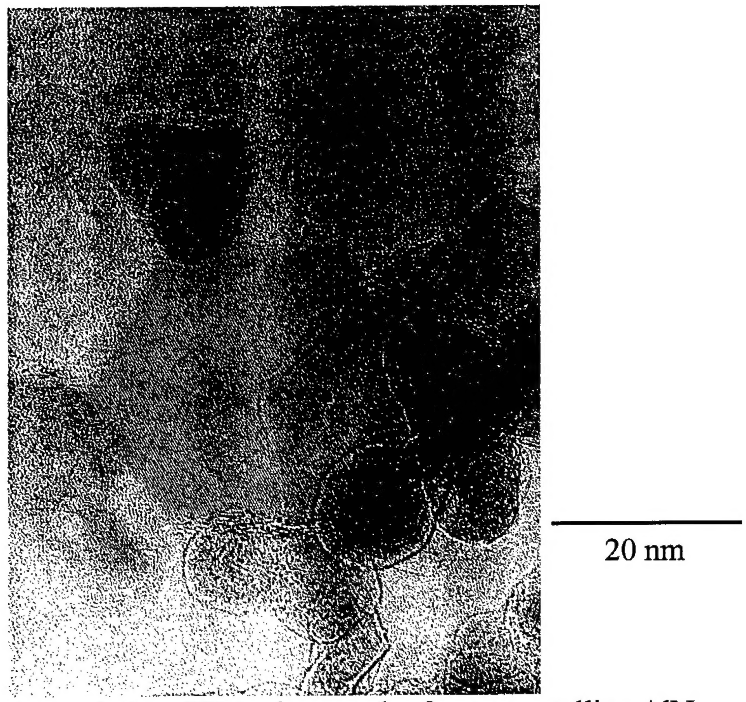

Figure 3. High-resolution TEM micrograph of nanocrystalline AlN.

1. A.C. Da Cruz, R.J. Munz, and H. Vali, "The Densification and Microstructure Development of Sintered Aluminum Nitride Ultrafine Powder Produced in a Two-Stage Transferred-Arc Plasma Reactor," *J. Mater. Sci. Lett.,* **17** [15] 1255-61 (1998).
2. J.P. Lecompte, J. Jarrige, and J. Mexmain, "Hot Pressing of Aluminum Nitride," pp. 293-99 in Progress in Nitrogen Ceramics, edited by F.L. Riley, Martinus Nijhoff Publishers, Boston, 1983.
3. K. Komeya and H. Inoue, "Sintering of Aluminum Nitride: Particle Size Dependence of Sintering Kinetics," *J. Mater. Sci.*, **4** 1045-50 (1969).
4. Y. Kurokawa, K. Utsumi, and H. Takamizawa, "Development and Microstructural Characterization of High-Thermal-Conductivity Aluminum Nitride Ceramics," *J. Am. Ceram. Soc.*, **71** [7] 588-94 (1988).
5. M.S. Sandlin, K.J. Bowman, and J. Root, "Texture Development in SiC-Seeded AlN," *Acta Mater.,* **45** [1] 383-96 (1997).